PB86-150620

Dioxin Emissions from Industrial Boilers Burning Hazardous Materials

Acurex Corp., Mountain View, CA

Prepared for

Environmental Protection Agency, Cincinnati, OH

Jan 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-150620

BEGIN FIRST LINE OF TEXT HERE
CENTER OF PAGE
TOP OF IMAGE AREA

EPA/600/2-85/118
January 1986

DIOXIN EMISSIONS FROM INDUSTRIAL BOILERS BURNING HAZARDOUS MATERIALS

DROPPED HEAD; BEGIN SECTIONS HERE

by

C. Castaldini
Acurex Corporation
Energy & Environmental Division
555 Clyde Avenue
P.O. Box 7555
Mountain View, CA 94039

and

Robert A. Olexsey
Research Program Manager
Alternative Technologies Division
Hazardous Waste Engineering Research Laboratory
Incineration Research Branch
Cincinnati, Ohio 45268

6-1/2"
9-1/8"

EPA Contract No. 68-03-3241

for

Hazardous Waste Engineering Research Laboratory
U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Cincinnati, Ohio 45268

BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 287)
TYPING GUIDE SHEET

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-85/118	2.
3. RECIPIENT'S ACCESSION NO. PB86 150620/AS	
4. TITLE AND SUBTITLE DIOXIN EMISSIONS FROM INDUSTRIAL BOILERS BURNING HAZARDOUS MATERIALS	5. REPORT DATE January 1986 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) C. Castaldini and Robert A. Olexsey	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Acurex Corporation 555 Clyde Avenue P. O. Box 7555 Mountain View, California 94039	10. PROGRAM ELEMENT NO. D109 11. CONTRACT/GRANT NO. 68-03-3241
12. SPONSORING AGENCY NAME AND ADDRESS U. S. Environmental Protection Agency Hazardous Waste Engineering Research Laboratory 26 West St. Clair Street Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/12
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

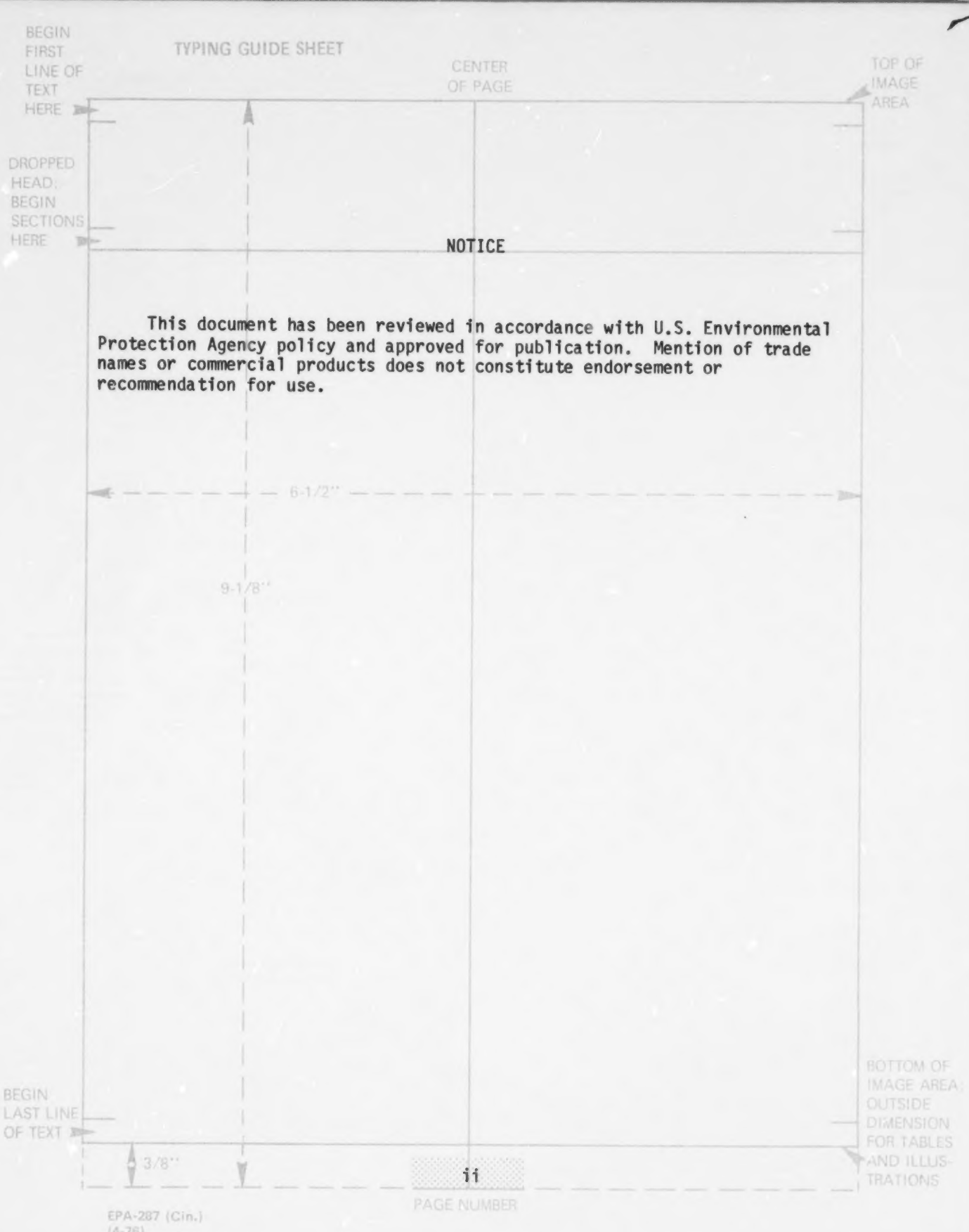
Laboratory analyses for polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo-furans (PCDF) were performed on waste fuels and stack gas emission samples from five industrial boiler test sites cofiring liquid hazardous wastes. Analytical results indicate that, apart from creosote sludge, chlorinated wastes were void of PCDD and PCDF compounds at detection limits in the range of 0.045 to 4.17 ppb. Creosote sludge cofired with wood waste in a stoker boiler was found to contain 7.4 ppm of total dioxins, primarily hepta and octa homologs. Stack gas concentrations of PCDD were highest for the creosote wood-fired stoker at about 75 ng/m^3. Other PCDD results indicate concentrations ranging from below detection levels (0.0022 ng/m^3 to 0.019 ng/m^3) to a maximum of 1.1 ng/m^3. PCDF concentrations were generally higher with total furan levels up to 5.5 ng/m^3. No 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD) was detected in any waste fuel. While the 2,3,7,8-TCDD isomer was detected in flue gas emissions from one boiler, the measured value for the emissions of 2,3,7,8-TCDD was equal to the detection limit for the compound in the particular flue gas (0.002 ng/m^3).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 38
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE



NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the need of both large and small businesses in handling their wastes responsibly and economically.

This report describes the results obtained from laboratory analyses of flue gas samples from industrial boilers burning hazardous waste materials. The purpose of the analyses was to determine if detectable quantities of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo-furans (PCDF) are emitted from such boilers when hazardous waste materials are burned. This information will be useful to regulatory officials who are responsible for setting standards, to permitting officials who may encounter questions about dioxin emissions during a permitting process and to members of the technical community who are seeking safe methods for hazardous waste disposal. For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

ABSTRACT

Laboratory analyses for polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo-furans (PCDF) were performed on waste fuels and stack gas emission samples from five industrial boiler test sites cofiring liquid hazardous waste fuels. Analytical results indicate that, apart from creosote sludge, chlorinated wastes were void of PCDD and PCDF homologs at detection limits in the range of 0.045 to 4.7 ppb. Creosote sludge cofired with wood waste in a stoker boiler was found to contain 7.4 ppm of total dioxins, primarily hepta and octa homologs. Stack gas concentrations of PCDD were highest for the creosote wood-fired stoker at about 75 ng/m^3. Other PCDD results indicate concentrations ranging from below detection levels (0.0022 to 0.019 ng/m^3) to a maximum of 1.1 ng/m^3. PCDF concentrations were generally higher with total furan levels up to 5.5 ng/m^3. No 2,3,7,8-tetrachlorodibenzo-p-dioxin was detected in any waste fuel. While the 2,3,7,8-TCDD isomer was detected in the flue gas emissions from one boiler, the measured value for the emissions of 2,3,7,8-TCDD was equal to the detection limit for the compound in the particular flue gas (0.002 ng/m^3).

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

CONTENTS

	Forward	iii
	Abstract	iv
	Tables	vi
1	Introduction	1
	1.1 Program Objective	1
2	Test Program Description	6
	2.1 Test Description	6
	2.2 Analysis Protocol	8
3	Results	10
4	Interpretation and Conclusion	16
	References	19
	Appendix A -- Battelle Columbus Laboratory Analytical Report	20

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

TABLES

Number		Page
1	Summary of Test Site Boilers	2
2	Summary of Test With Waste Fuel Firing	3
3	Summary of Test Average DRE's for Volatile POHC's	4
4	Test Sites Selected for PCDD and PCDF Analyses	7
5	Dioxins Concentrations in Waste Fuels	11
6	Furan Concentrations in Waste Fuels	12
7	Flue Gas Concentrations -- Dioxins	13
8	Flue Gas Concentrations -- Furans	14
9	QA/QC Results for Flue Gas Sample Extracts	15
10	Site A Dioxin DRE's.	17
11	Mass Flow Rates of Total Dioxins and Furans	18

6 1/2"
9 1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

SECTION 1

INTRODUCTION

In 1982, the EPA's Hazardous Waste Engineering Research Laboratory in Cincinnati initiated a series of field test programs on industrial boilers cofiring hazardous wastes. A principal objective of these tests was to develop a data base on the destruction and removal efficiencies (DRE) of industrial boilers co-firing hazardous organic components in waste fuels. This data base was required by the EPA's Office of Solid Waste and Emergency Response to evaluate hazards and potential control measures in preparation for recommending regulations controlling ongoing industry cofire practices.

Eleven boilers were tested under typical industrial operating conditions. The boiler specifications for these 11 tests are listed in Table 1. Waste specifications and additional boiler specifications are listed in Table 2. The majority of the tests were on gas- and oil-fired watertube boilers which correspond to the predominant cofiring application in industry. The wastes at Sites E through K were spiked with carbon tetrachloride and, usually, chlorobenzene and trichloroethylene. This was done to extend the range of volatile POHC's to be monitored and to provide a common basis for intra-boiler comparisons.

Table 3 summarizes the DRE results for volatile principal organic hazardous compounds (POHC's). With the exception of Site F, site-average DRE's exceeded 99.99 percent. The mass-weighted volatile organics DRE for all test sites was 99.998 percent. Additional results for the Site A stoker, however, indicated DRE's lower than 99.99 percent for several semivolatile POHC's including pentachlorophenol and polynuclear aromatics in the creosote sludge. Generally, lower DRE's were attributed to nonsteady or transient combustion conditions.

Recently, additional tests were performed to measure volatile POHC DRE's and volatile PIC emissions during nonsteady and transient boiler operations typical for these combustion devices. These tests, documented in the Site L report (Ref. 2), indicate generally good destruction efficiency (DRE average 99.998 percent) under most nonsteady and off-specification combustion conditions investigated.

1.1 PROGRAM OBJECTIVE

The objective of this program was to perform laboratory analyses of boiler flue gas samples to determine concentrations of polychlorinated

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

TABLE 1. SUMMARY OF TEST SITE BOILERS (Source: Ref. 1)

Site	Boiler type	Steam capacity, kg/s (10^3 lb/hr)		Furnace volume, m^3 (ft^3)		Furnace waterwall surface, m^2 (ft^2)		Primary fuel	Number of burners (injection ports)	Typical waste fuels	Injection mechanism	Control device	Typical operation
A	Watertube stoker	1.3	(10)	17.4	(613)	106	(1,144)	Wood waste	2	Creosote sludge	Mixed with wood	Multicyclone	Fluctuating loads, combustion air and waste feed
B	Packaged firetube	1.1	(8.5)	1.1	(39)	8.0	(83)	Natural gas	1	Alkyd wastewater	Air atomized oil gun	None	Low boiler load. Maximum waste fire rate of 42 ml/s (40 gph)
C	Field-erected watertube	29	(230)	322	(11,400)	170	(1,800)	Natural gas or oil	6	Phenolic waste	One or two steam atomized burners	None	Low load with reduced number of burners. High excess air.
D	Field-erected converted watertube stoker	11.4	(90)	62	(2,200)	140	(1,520)	No. 6 oil	4	Methanol and toluene wastes with chlorinated organics	One of the lower level steam atomized burners	None	About 50 percent capacity with 3 or 4 burners in service
E	Packaged watertube	13.9	(110)	42	(1,480)	665	(7,160)	No. 6 oil	1	Methylmethacrylate byproduct wastes	Two steam atomized waste guns in main burner throat	None	Part load with maximum 250 ml/s (240 gph) waste firing rate for loads above 50 percent
F	Field-erected converted watertube	7.6	(60)	96	(3,390)	100	(1,100)	No. 6 oil, gas, or propane	2	Paint solvents	Lower steam atomized oil burner	None	Part load with maximum 190 ml/s (180 gph) waste firing rate for loads above 50 percent
G	Modified packaged firetube	5.0	(40)	6.4	(226)	20	(220)	None	1	Highly chlorinated organics	Available air atomized oil gun	2 scrubbers in series	Part load with startup on natural gas. Total chlorine up to 80 percent of waste fuel.
H	Field erected tangentially fired watertube	32	(250)	520	(18,400)	515	(5,540)	Pulverized coal	12 coal, 6 oil	Methyl acetate waste fuel	One or two steam atomized oil burners	ESP	At boiler capacity with maximum 440 ml/s (420 gph) waste firing rate
I	Packaged watertube	7.9	(62)	41	(1,430)	76	(820)	Natural gas	2	Aniline waste high in nitrate organics	Either upper or lower steam atomized burner	None	Staged combustion for low NO_x with maximum 130 ml/s (120 gph) waste flow
J	Packaged firetube	1.3	(10)	1.5	(51)	2.6	(91)	None	1	Artificially blended fuels	Available oil burner	None	Typical excess air of 17 percent
K	Packaged watertube	7.6	(60)	65	(2,270)	47	(508)	No. 6 oil	1	Blended waste with light oil	Mixed with heavy oil	None	Typical 70/30 percent heavy and light oil mixture

TABLE 2. SUMMARY OF TEST WITH WASTE FUEL FIRING (Source: Ref. 1)

Site	Number of waste-fuel-fired tests	Volumetric heat release rate, kW/m^3 (10^3 Btu/hr-ft^3)	Surface heat release rate, kW/m^2 (10^3 Btu/hr-ft^2)	Bulk furnace[a] temperature, °C (°F)	Bulk furnace[a] residence time, sec	Waste fuel heating value, MJ/kg (10^3 Btu/lb)	Waste heat input, percent of total	POHC's of interest
A	4	300 (29)	48 (16)	1,370 (2,500)	1.2	39 (17)	40	Phenol, pentachlorophenol, naphthalene fluorene, 2-4-Dimethylphenol
B	3	745 (72)	106 (34)	1,320 (2,400)	0.8	0.03-0.18 (0.013-0.077)	<1	Toluene
C	3	78 (7.5)	150 (48)	1,320 (2,400)	2.0	39 (17)	38	Phenol
D	3	400 (39)	180 (57)	1,430 (2,600)	1.1	21 (8.8)	18	Tetrachloroethylene
	3	230 (22)	100 (33)	1,370 (2,500)	1.3	42 (18)	48	Bis(2-chloroethyl)ether, toluene
E	1	580 (55)	37 (11)	1,550 (2,800)	0.7	27 (12)	22	Methylmethacrylate, α-hydroxy methyl isobuty-rate and α-hydroxy isobutyrate methyl ether
	6	380-770 (37-74)	24-49 (7.6-15)	1,480-1,590 (2,700-2,900)	0.5-1.0	25-27 (11-12)	19-43	Above plus carbon tetrachloride, chlorobenzene and trichloroethylene
	1	420 (40)	26 (8.1)	1,480 (2,700)	1.1	37 (16)	56	Toluene, methylmethacrylate
F	3	114 (11)	104 (34)	1,370 (2,500)	2.0	33 (14)	9.0	Carbon tetrachloride, chlorobenzene, trichloroethylene, toluene
G	3	820 (79)	262 (81)	1,350 (2,450)	0.4	21 (9.0)	100	Carbon tetrachloride, epichlorohydrin, bis(2-chloroisopropyl)ether
H	3	180 (17)	183 (58)	1,370 (2,500)	2.0	17 (7.0)	2.4-4.3	Carbon tetrachloride, chlorobenzene, 1,1,1-Trichloroethane
I	2	340 (33)	180 (57)	1,430 (2,600)	1.8	25 (11)	8.2	Carbon tetrachloride, chlorobenzene, trichloroethylene, toluene, aniline, benzene, nitrobenzene
J	6	690-1,750 (65-170)	118-300 (37-95)	1,310-1,370 (2,400-2,500)	0.3-0.7	42 (18)	100	Carbon tetrachloride, chlorobenzene, trichloroethylene, toluene
K	1	270 (26)	370 (120)	1,370 (2,500)	1.8	40 (17)	65	Carbon tetrachloride, chlorobenzene, trichloroethylene, toluene, benzene

[a]Not measured values. Estimates of bulk gas temperature in the furnace were used to calculate bulk furnace residence time. Values to be considered approximate.

TABLE 3. SUMMARY OF TEST AVERAGE DRE'S FOR VOLATILE POHC'S[a] (Source Ref. 1)

POHC	Site B	Site D	Site E	Site F	Site G	Site H	Site I	Site J	Site K	Range	Weighted average
Carbon tetrachloride			99.9990- 99.9998 (99.9996)[b]	99.98- 99.9990 (99.995)	99.995- 99.9990 (99.998)	99.97- 99.9994 (99.98)	99.9990- 99.9993 (99.9993)	99.997- 99.9998 (99.9990)	99.9998	99.97- 99.9998	99.9992
Trichloroethylene			99.994- 99.9995 (99.998)	99.98- 99.998 (99.996)			99.99990- 99.99992 (99.99991)	99.998- 99.99993 (99.9996)	99.99990	99.98- 99.99993	99.9994
1,1,1-Trichloroethane						99.97- 99.9996 (99.994)				99.97- 99.9996	99.994
Chlorobenzene			99.995- 99.99990 (99.998)	99.96- 99.992 (99.98)		99.990- 99.997 (99.992)	99.997- 99.9990 (99.998)	99.8- 99.97 (99.95)	99.99992	99.8- 99.99992	99.992
Benzene							99.97- 99.98 (99.97)		99.996	99.97- 99.996	99.990
Toluene	99.991	99.9992- 99.99990 (99.9996)	99.997	99.90- 99.97 (99.95)			99.998	99.9990- 99.9997 (99.9990)	99.99996	99.90- 99.99996	99.998
Tetrachloroethylene		99.994- 99.9992 (99.998)								99.994- 99.9992	99.998
Methylmethacrylate			99.95- 99.997 (99.991)							99.95- 99.995	99.991
Mass weighted average	99.991	99.994- 99.99990 (99.9993)	99.95- 99.99990 (99.995)	99.90- 99.9990 (99.98)	99.995- 99.9990 (99.998)	99.97- 99.9996 (99.991)	99.97- 99.99992 (99.998)	99.8- 99.99993 (99.9990)	99.996- 99.99996 (99.9997)	99.8- 99.99996	99.998

[a]Each test average DRE is generally based on the weighted average of triplicate measurements.
[b]Numbers in parentheses represent the site-specific POHC average DRE.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE
6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA: OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo-furans (PCDF) including the 2,3,7,8 tetra isomer for selected boiler sites. In addition, analyses of waste fuels cofired at these selected test sites were also performed to determine whether PCDD and PCDF emissions could be attributed to waste fuels or to products of combustion of waste fuels.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE

SECTION 2

TEST PROGRAM DESCRIPTION

2.1 TEST DESCRIPTION

Table 4 lists test sites selected for PCDD and PCDF analyses. At Site A, four cofire tests were performed by burning a mixture of wood waste (chips, bark, and sawdust) with creosote sludge. The sludge contained phenolic coupounds including pentachlorophenol, generally identified as a precursor to dioxin emissions during combustion. Heat input attributed to the creosote sludge was estimated at 40 percent for these tests. Operation of the stoker at Site A was erratic with large and frequent fluctuations in excess air and CO emissions. This operation is typical of batch-feed wood-fired stokers.

Two test series were performed at Site D, each consisting of three cofired tests. A methanol waste stream containing tetrachloroethylene was burned with residual oil in a multiburner boiler. Heat input contribution due to the methanol waste ranged between 18 and 30 percent. A toluene waste stream containing bis(2-chloroethyl)ether was cofired in the second test series contributing about 47 percent of the total heat input to the boiler. Boiler operation during the initial test series (D1) was characterized by several burner upsets caused by waste feed problems. Boiler heat input, and thus, furnace temperature, was higher for D1 tests than for the D2 test series.

A methylmethacrylate waste stream containing spiked amounts of carbon tetrachloride, chlorobenzene and trichloroethylene was cofired at Site E during a test series involving six individual cofire tests. With the exception of one, all tests were conducted with residual oil as the primary fuel. Natural gas was substituted for residual oil during one of the tests. Three different boiler heat input rates were investigated. The waste stream contributed from 20 to 43 percent of the total heat input. Boiler operation was relatively steady for each test condition.

The pulverized coal-fired boiler at Site H was cofired with methyl acetate waste spiked with carbon tetrachloride, chlorobenzene and 1,1,1-trichloroethane. The boiler was fired at capacity with the waste contributing only 2.4 to 4.3 percent of the total heat input. Boiler operation was steady during all three cofired tests.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

TABLE 4. TEST SITES SELECTED FOR PCDD AND PCDF ANALYSES

Site ID	Boiler type	Primary fuel	Waste fuel	Waste fuel POHC's	concentration (mg/ml)	Number of tests	Streams analyzed for PCDD and PCDF
A	Watertube stoker	Wood chips sawdust	Creosote sludge	Phenol	0.6 to 1.3	Four cofire tests	• Creosote waste
				Pentachlorophenol	2.2 to 6.0		• Flue gas
				Naphthalene	5.4 to 19		• Flyash from multiclone
				Fluorene	4.4 to 7.6		• Bottom ash
				2,4-Dimethylphenol	0.3 to 1.3		
D1	Field erected converted watertube stoker	No. 6 fuel oil	Methanol waste	Tetrachloroethylene	46 to 310	Three cofire tests	• Waste fuel • Flue gas
D2		No. 6 fuel oil	Toluene waste	Bis(2-chloroethyl)ether	39 to 42	Three cofire tests	• Waste fuel • Flue gas
				Toluene	950		
E	Packaged watertube	No. 6 fuel oil[a]	Methylmethacrylate waste artificially spiked	Methylmethacrylate	33 to 52	Six cofire tests	• Waste fuel • Flue gas
				Carbon tetrachloride	27 to 34		
				Chlorobenzene	16 to 20		
				Trichloroethylene	27 to 32		
H	Field erected watertube	Pulverized coal	Methyl acetate waste artificially spiked	Carbon tetrachloride	24 to 51	Three cofire tests	• Waste fuel • Flue gas
				Chlorobenzene	26 to 53		
				1,1,1-Trichloroethane	20 to 41		
L	Packaged watertube	Natural gas	Methylmethacrylate waste artificially spiked	Carbon tetrachloride	6.8	One test	• Waste fuel • Flue gas
				Chlorobenzene	15		

[a]One of the six tests was performed with natural gas as the primary fuel

BEGIN LAST LINE OF TEXT
3/8"
7
PAGE NUMBER
EPA-257 (Cin.) (4-76)
BOTTOM OF IMAGE AREA. OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
DROPPED HEAD. BEGIN SECTIONS HERE
BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

Sampling for semivolatile and nonvolatile organics at Site L was performed only during one cofire test. Carbon tetrachloride and chlorobenzene spiked methylmethacrylate waste was burned with natural gas. Heat input from the waste was approximately 30 percent with steady boiler operations. Although several other nonsteady tests were performed at Site L, none of the measurements included protocols for semivolatile and nonvolatile organic compounds.

2.2 ANALYSIS PROTOCOL

Analysis for PCDD and PCDF including the isomers 2,3,7,8-TCDD and -TCDF were performed by Battelle Columbus Laboratory (BCL) on both waste fuels and flue gas samples corresponding to the test series listed in Table 4. The analytical method by BCL was based on high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). Detection limits were on the order of 0.04 to 0.13 ng/ml (ppb) for tetra isomers and 1 to 4 ppb for octa isomers in the waste fuels. Detection limits for flue gas samples ranged between 0.005 to 0.08 ng/m^3 of gas (about 0.0003 to 0.0005 ppt(v)).

Quality assurance procedures included recovery analysis of spiked internal standards and analytical method blanks. Appendix A details the analytical procedures and results obtained. Soxhlet extraction of flue gas samples collected using the modified EPA Method 5 train were performed by the Acurex Laboratory using the procedure depicted in Figure 1. These extract samples were in turn composited and analyzed by BCL.

Analyses focused on both waste fuels and flue gas samples. However, for Site A, selected ash samples collected from the stoker bottom hopper and from the multiclone hopper were also analyzed. PCDD analysis results of ash streams documented in Reference 3 are not reported here. For each of the Site D, E, and H test series listed in Table 4, waste fuels were composited into one sample and analyzed. Similarly, organic extracts of flue gas samples for each test series were composited and analyzed.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-70)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

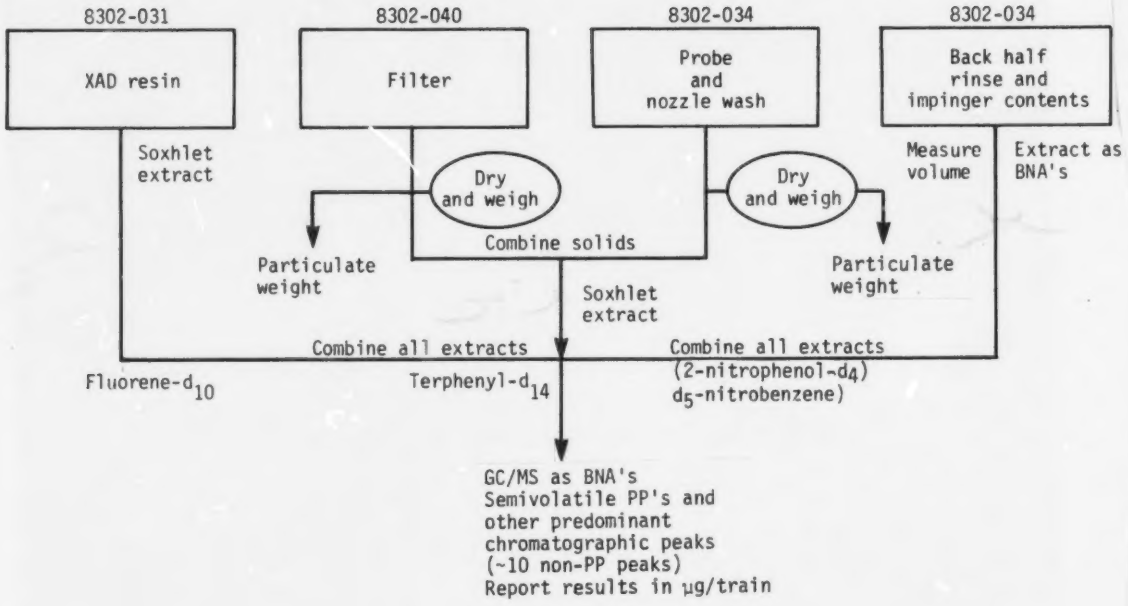


Figure 1. Flow scheme for extraction and analysis of organic samples from MM5 trains.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

SECTION 3

RESULTS

Tables 5 and 6 summarize dioxins and furans concentrations, respectively, in the waste fuels at each of the test sites selected for these analyses. Site A results are based on an individual sample of the creosote collected during test 2. As indicated, all waste fuels, with the exception of Site A, were void of PCDD's or PCDF's at detection limits indicated in the tables' footnotes. Site A creosote contained about 7.4 ppm total PCDD's, primarily hepta and octa isomers. No PCDF analysis was performed on the Site A creosote sludge since the sample was exhausted in the PCDD analysis. The highly toxic 2,3,7,8-TCDD was not detected in any of the waste fuels.

Tables 7 and 8 summarize flue gas concentrations of PCDD and PCDF homologs, respectively. Site A emissions measured during two tests showed total PCDD of about 75 ng/m^3, by far the highest level of any of the other test sites. Total PCDD at Site D measured 0.80 and 0.64 ng/m^3 for the two test series, respectively. Minute levels of 2,3,7,8-TCDD were detected in the sample for the D2 test series when cofiring with toluene and bis(2-chloroethyl)ether. However, the concentration was at the detection limit. Both Site E and H emissions indicate no PCDD emissions. However, flue gas samples obtained at Site L showed 1.1 ng/m^3 total PCDD, primarily tetra isomers.

PCDF emissions were generally higher than PCDD emissions. Emissions were lowest for the test series at Site E and highest for the test series D1 and L. No PCDF data are available for Site A.

In general, flue gas concentrations of total PCDD and PCDF compounds ranged between non-detected (below 0.08 ng/m^3) to 5.5 ng/m^3 with the exception of the wood/creosote stoker. These concentrations correspond to a maximum of about 0.3 ppt(v).

Table 9 summarizes the results of XAD-2 sorbent analytical blank extracts and the results of analysis of a field XAD blank from the Site L test program. Results indicate below-detection levels of PCDD and PCDF homologs in all samples except the Site L field blank which showed 3.77 ng of TCDD. This compound was tentatively identified as a 1,2,3,4-TCDD isomer. The presence of the 1,2,3,4-TCDD in the field blank sample could not be explained and thus is to be considered an artifact of the analytical procedure.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

TABLE 5. DIOXIN CONCENTRATIONS IN WASTE FUELS (ppb)

Site identification	Sample description	Tetra	Penta	Hexa	Hepta	Octa	Total PCDD	2,3,7,8-TCDD
A	Test 2 creosote sludge	ND	2.1	360	3,600	3,400	7,400	ND
D1	Composited of methanol/ PCE for tests 2, 3, and 4	ND	ND	ND	ND	ND	ND	ND
D2	Composited of toluene/ BCEE for tests 5, 6, and 7	ND	ND	ND	ND	ND	ND	ND
E	Composited of MMA CCl_4, TCE, and Clϕ for tests 3, 4, 5, 6, 7, and 8	ND	ND	ND	ND	ND	ND	ND
H	Composited of methyl acetate, CCl_4, Clϕ and 1,1,1-TCA for tests 2, 3, and 4	ND	ND	ND	ND	ND	ND	ND
L	Test 2 MMA, CCl_4 and Clϕ	ND	ND	ND	ND	ND	ND	ND
	Analytical method blank	ND	ND	ND	ND	ND	ND	ND

Note
ND -- Not detected. Below detection limits. Detection limits in the range of 0.045 to 4.17 ppb. Detection limits are summarized in Appendix A, Table 4, Page 30

TABLE 6. FURAN CONCENTRATIONS IN WASTE FUELS (ppb)

Site identification	Sample description	Tetra	Penta	Hexa	Hepta	Octa	Total PCDF	2,3,7,8-TCDF
D1	Composites of methanol/ PCE for tests 2, 3, and 4	ND	ND	ND	ND	ND	ND	ND
D2	Composites of toluene/ BCEE for tests 5, 6, and 7	ND	ND	ND	ND	ND	ND	ND
E	Composited of MMA, CCl_4 TCE and CLϕ for tests 3, 4, 5, 6, 7, and 8	ND	ND	ND	ND	ND	ND	ND
H	Composited of methyl acetate CCl_4, CIϕ and 1,1,1-TCA for tests 2, 3, and 4	ND	ND	ND	ND	ND	ND	ND
L	Test 2 MMA, CCl_4 and CIϕ	ND	ND	ND	ND	ND	ND	ND
	Analytical blank	ND	ND	ND	ND	ND	ND	ND

Note
ND -- Not detected. Below detection limits. Detection limits in the range of 0.045 to 2.0 ppb. Detection limits are summarized in Appendix A, Table 3, Page 29

BEGIN LAST LINE OF TEXT
3/8"
EPA-287 (Cin.) (4-76)
PAGE NUMBER 12
TABLES AND ILLUSTRATIONS
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES
DROPPED HEAD: BEGIN SECTIONS HERE
BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA

TABLE 7. FLUE GAS CONCENTRATIONS -- DIOXINS (ng/m^3)

Site identification	Sample description	Flue gas sample (m^3)	Tetra	Penta	Hexa	Hepta	Octa	Total PCDD	2,3,7,8-TCDD
A	Test 2 MM5 extract	2.34	43	14	7.5	5.5	4.6	75	ND
	Test 4 MM5 extract	2.50	38	24	12	1.6	0.8	76	ND
D1	Composited of MM5 extracts for test 2, 3, and 4	27.8[a]	0.12	0.074	0.10	0.25	0.26	0.80	ND
D2	Composited of MM5 extracts for tests 5, 6, and 7	18.4[a]	0.027	0.032	0.052	0.12	0.41	0.64	0.002[b]
E	Composited of MM5 extracts for tests 3, 4, 5, 6, 7, and 8	51.5[a]	ND	ND	ND	ND	ND	ND	ND
H	Composited of MM5 extracts for tests 2, 3, and 4	26.0[a]	ND	ND	ND	ND	ND	ND	ND
L	Test 2 MM5 extract	8.7	0.57	0.010	0.066	0.12	0.29	1.1	ND

[a]Composited sample volumes
[b]Measured value was equal to the detection limit

Note
ND -- Not detected. Detection limit 0.005 to 0.08 ng/m^3
To convert ng/m^3 to ppt multiply table entries by 0.068 for tetra, 0.062 for penta, 0.056 for hexa, 0.052 for hepta and 0.048 for octa

BEGIN LAST LINE OF TEXT
EPA-287 (Clm.) (4-75)
3/8"
PAGE NUMBER 13
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
DROPPED HEAD; BEGIN SECTIONS HERE
BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA

TABLE 8. FLUE GAS CONCENTRATIONS -- FURANS (ng/m^3)

Site identification	Sample description	Flue gas sample (m^3)	Tetra	Penta	Hexa	Hepta	Octa	Total PCDF	2,3,7,8-TCDF
D1	Composited of MM5 extracts for tests 2, 3, and 4	27.8[a]	2.1	1.4	0.77	0.94	0.27	5.5	0.24
D2	Composited of MM5 extracts for tests 5, 6, and 7	18.4[a]	0.10	0.035	ND	0.034	0.07	0.24	0.13
E	Composited of MM5 extracts for tests 3, 4, 5, 6, 7, and 8	51.5[a]	0.12	0.019	ND	ND	ND	0.14	0.014
H	Composited of MM5 extracts for tests 2, 3, and 4	26.0[a]	ND	0.14	0.39	0.077	0.20	0.81	ND
L	Test 2 MM5 extract	8.7	0.61	0.53	0.62	0.38	0.34	2.5	0.033

[a]Composited sample volumes

Note
ND -- Not detected. Detection limit 0.005 to 0.037 ng/m^3
To convert ng/m^3 to ppt, multiply table entries by 0.072 for tetra, 0.065 for penta, 0.059 for hexa, 0.054 for hepta, and 0.050 for octa

BEGIN LAST LINE OF TEXT
3/8"
EPA-287 (Cin.) (4-76)
PAGE NUMBER
14
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
DROPPED HEAD; BEGIN SECTIONS HERE
BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

TABLE 9. QA/QC RESULTS FOR FLUE GAS SAMPLE EXTRACTS (ng)

		Tetra	Penta	Hexa	Hepta	Octa	2,3,7,8-Tetra
Method blank	PCDD	ND	ND	ND	ND	ND	ND
	PCDF	ND	ND	ND	ND	ND	ND
Site L field blank	PCDD	3.77	ND	ND	ND	ND	ND
	PCDF	ND	ND	ND	ND	ND	ND

Note
ND -- Not detected; detection limit in the range of 0.040 to 1.50 ng in each extract sample

9-1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

SECTION 4

INTERPRETATION AND CONCLUSION

Site A creosote sludge was the only waste fuel found to contain dioxins in detectable quantities. Table 10 summarizes the DRE of each dioxin homolog and for the 2,3,7,8-TCDD at Site A. In the creosote waste, dioxin tended to predominate in the higher homologs -- hepta and octa. In the flue gas, the reverse is evident; dioxin concentrations tended toward the lower homologs -- tetra and penta. A plausible interpretation is that during combustion the higher homologs in the waste were reduced to lower homologs which were emitted in the flue gas. This would account for the low DRE (negative in the case of tetra-CDD) for the lower homologs.

Table 11 summarizes the mass flow rates for total dioxins and total furans for the test series D1, D2, E, H, and L. The calculated input rates are based on the combined waste firing rate for the test series and the sums of the detection limits for total PCDD and total PCDF. The flue gas emission rate was calculated using the combined flue gas emission rate for each test series since sample extracts were composited and analyzed as one sample. The table indicates that input rates of dioxins and furans were not necessarily below the measured flue gas emission rate. Therefore, although no dioxins and furans were detected in each waste stream, it cannot be stated with certainty that measured dioxins and furans in the flue gas were products of combustion.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE
11 1/2"
9 1/8"
BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.) (4-76)

TABLE 10. SITE A DIOXIN DRE'S

Homolog/ Isomer	Flowrates (µg/sec) Creosote	Flue gas	DRE (percent)
2,3,7,8-TCDD	ND	ND	NA
Tetra-CDD	ND	0.14	
Penta-CDD	0.1	0.044	56.0
Hexa-CDD	18	0.024	99.87
Hepta-CDD	180	0.017	99.99
Octa-CDD	170	0.014	99.99
Total-CDD	370	0.24	99.94

Note
NA -- not applicable, DRE cannot be computed because concentration in both input and flue gas streams were below the detection limit
ND -- not detected; below the detection limits of 0.0032 for creosote and 0.0047 for the flue gas

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

TABLE 11. MASS FLOW RATES OF TOTAL DIOXINS AND FURANS

Site	Total PCDD		Total PCDF	
	Input rate[a] (ng/s)	Emission rate[a] (ng/s)	Input rate[a] (ng/s)	Emission rate[a] (ng/s)
D_1	ND (2,400)	22	ND (2,500)	150
D_2	ND (3,600)	12	ND (1,800)	4.4
E	ND (5,100)	ND (4.2)	ND (3,300)	7.4
H	ND (20)	ND (2.7)	ND (17)	27
L	ND (560)	7.4	ND (570)	17

[a]Based on firing rate of waste and sum of detection limits for total PCDD and total PCDF listed in Appendix A, Table 3 and 4.

6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

EPA-287 (Cin.)
(4-76)

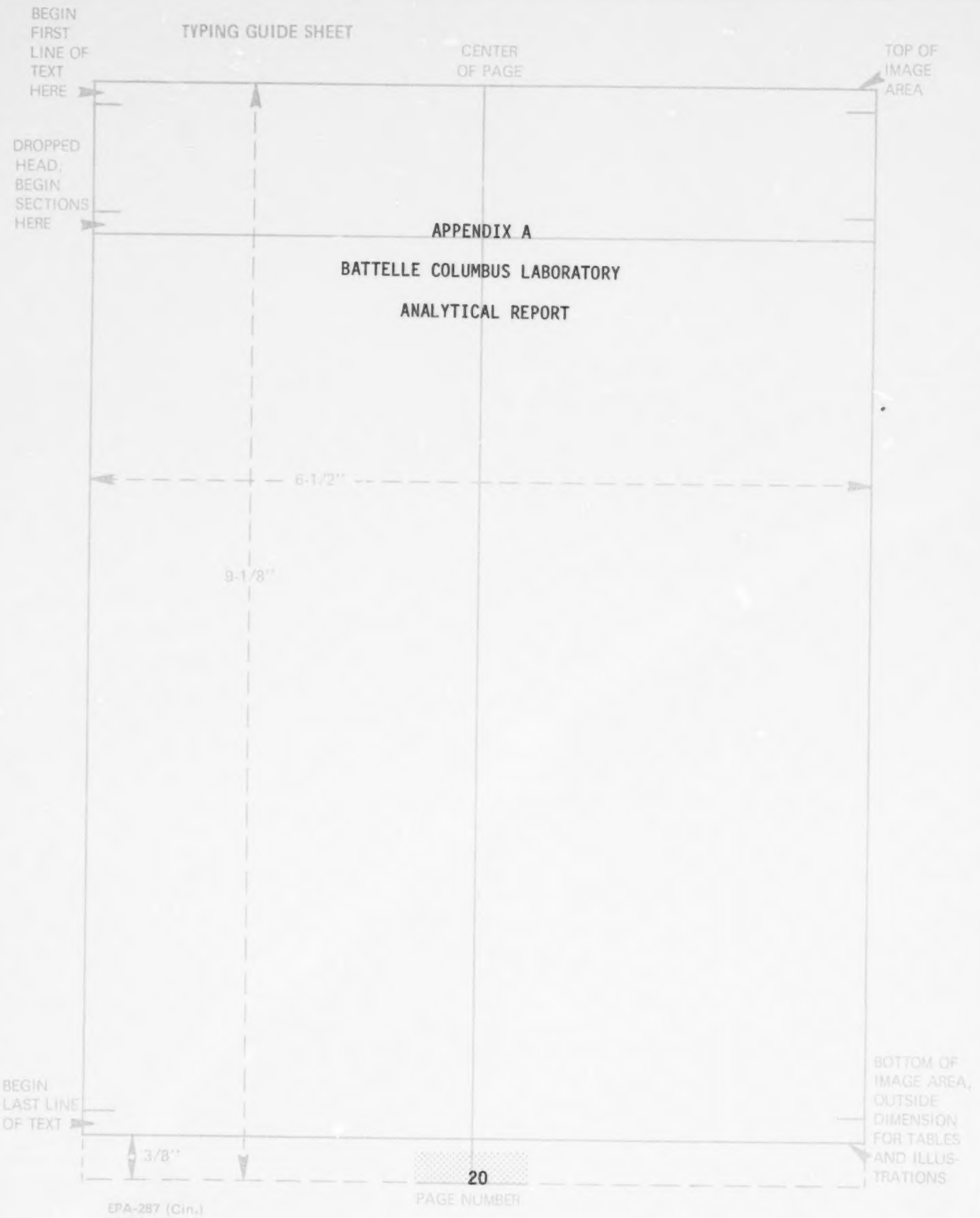
BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE
6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

REFERENCES

1. Castaldini, et al., "Engineering Assessment Report Hazardous Waste Cofiring in Industrial Boilers," Acurex Technical Report TR-84-159/EED, June 1984.

2. DeRosier, R., et al., "Emission Testing of Industrial Boilers Cofiring Hazardous Wastes -- Site L," Acurex Technical Report, December 1984.

3. Castaldini, C., et al., "Emission Testing of Industrial Boilers Cofiring Hazardous Wastes -- Site A," Acurex Technical Report TR-83-112/EED, January 1983.


BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE
APPENDIX A
BATTELLE COLUMBUS LABORATORY
ANALYTICAL REPORT
6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
20
PAGE NUMBER
EPA-287 (Cin.) (4-76)

Battelle
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201-2693
Telephone (614) 424-6424
Telex 24-5454

January 25, 1985

Mr. Carlo Castaldini
Project Engineer
Acurex Corporation
555 Clyde Avenue
P.O. Box 7555
Mountain View, CA 94039

Dear Mr. Castaldini:

We have completed the analyses of the fuel oils and XAD-2 resin extract samples. I am enclosing a description of the analytical methodology, the instrumentation, and the quality assurance measures that we employed. Copies of the computer generated selected ion chromatograms are included in the appendix. Please contact me at (614) 424-4247 if you have any questions.

Sincerely,

Fred L. DeRoos

Fred L. DeRoos, Ph.D.
Principal Research Scientist
Analytical Chemistry Section

FLD/bsf

Analytical Methodology

Introduction

This report describes the analytical procedures used to determine the levels of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in eleven composite samples from Acurex Corporation, Mountain View, California. The samples, consisting of fuel oils and XAD-2 extracts, were received by Battelle on December 14, 1984.

Extraction

The composited fuel oil samples were prepared by combining 5 ml of each of the fuel samples specified in your letter dated December 7, 1984. One milliliter of the composite fuel sample was removed for sample extraction and was spiked with three isotopically labelled internal standards. The internal standard spikes were 25 ng of 2,3,7,8-tetrachlorodibenzofuran-$^{13}C_{12}$ (2,3,7,8-TCDF-$^{13}C_{12}$), 25 ng of 2,3,7,8-tetrachlorodibenzo-p-dioxin-$^{13}C_{12}$ (2,3,7,8-TCDD-$^{13}C_{12}$), and 25 ng of octachlorodibenzo--p-dioxin-$^{13}C_{12}$ (OCDD-$^{13}C_{12}$). The samples were diluted with 30 ml of hexane and washed multiple times with concentrated sulfuric acid. The hexane solution was then concentrated to 10 ml and eluted through a 5 g basic alumina column using 25 ml of hexane, 25 ml of 3% methylene chloride/hexane, and 25 ml of 50% methylene chloride/hexane. The 50% methylene chloride/hexane fraction was collected, concentrated and exchanged into hexane. The sample was then passed through a multilayer silica gel column containing 1 g silica gel, 2 g 33% NaOH on silica gel, 1 g silica gel, 4 g 44% H_2SO_4 on silica gel and 2 g silica gel. The eluate was collected, concentrated, solvent exchanged into hexane, and passed through a 1 g basic alumina column. The eluting solvents were 5 ml of hexane, 5 ml of 3% methylene chloride/hexane and 22 ml

of 50% methylene chloride/hexane. The 50% methylene chloride/hexane fraction was collected, concentrated to dryness and diluted with 20 µl of decane.

Composite samples of the XAD-2 extracts were prepared by combining all of the specified samples. One of the 6 sets of samples that were combined, XE38, was prepared with methylene chloride since the samples to combine were dry. The composite XAD-2 samples were spiked with 25 ng 2,3,7,8-TCDF-$^{13}C_{12}$, 25 ng 2,3,7,8-TCDD-$^{13}C_{12}$ and 25 ng OCDD-$^{13}C_{12}$ and eluted through two silica gel columns. The first column contained 10 g of 44% concentrated H_2SO_4 on silica gel and the second was a multilayer silica gel column as described above. The eluate was collected, concentrated to 5 ml, and passed through a 1 g basic alumina column. The elution solvents were 5 ml of hexane, 5 ml of 3% methylene chloride/hexane, and 22 ml of 50% methylene chloride/hexane. The 50% methylene chloride/hexane fraction was collected, concentrated to dryness and diluted with 20 µl of decane.

Analysis

The extracts were analyzed and quantified for PCDD/PCDF using combined capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The HRGC/HRMS consisted of a Carlo Erba Model 4160 gas chromatograph interfaced directly into the ion source of a VG Model 7070 mass spectrometer. The primary chromatographic column was a 30M DB-5 fused silica column using helium carrier gas at a flow velocity of 25 cm/sec. The mass spectrometer was operated in the electron impact (EI) ionization mode at a mass resolution of 9000-12000 (M/ΔM, 10% valley definition). The operating parameters of the HRGC/HRMS are summarized in Table 1. The primary analyses, determination of total level of each PCDD/PCDF class, were carried out using two separate HRGC/HRMS runs. This approach was necessary due to chromatographic

overlap of adjacent isomer classes and hardware limitations to the number of masses that could be sequentially monitored. The first run provided data for the PCDD and PCDF isomers having an odd number of chlorine substituents, while the second run determined the levels of the isomers containing an even number of chlorines. Although the DB-5 capillary column is excellent for PCDD/PCDF isomer class determinations, it does not provide the isomer specificity of the more polar phase columns. Since 2,3,7,8-TCDD and 2,3,7,8-TCDF are the most toxic PCDD/PCDF isomers, all samples that were found to contain these isomers, using the DB-5 column, were reanalyzed using 50M CP Sil-88 fused silica capillary column which resolves 2,3,7,8-TCDD from the other 21 TCDD isomers. While this column does not provide complete separation of 2,3,7,8-TCDF, the level of confidence is far greater than with the DB-5 column and is considered to be state of the art. All HRGC/HRMS data were acquired by multiple-ion-detection using a VG Model 2035 Data System. The exact masses that were monitored are shown in Table 2.

Quality Assurance

The operation of the HRGC/HRMS was evaluated each day by analyzing standard mixtures of PCDD/PCDF isomers. These consisted of 2,3,7,8-TCDF, 2,3,7,8-TCDD, 2,3,7,8-TCDF-$^{13}C_{12}$, and 2,3,7,8-TCDD-$^{13}C_{12}$ mixtures to evaluate accuracy of quantification, mixtures of selected PCDD/PCDF isomers to evaluate the stability of the chromatographic elution windows, and TCDD isomer mixtures to evaluate isomer resolution. The mass accuracy of the MID unit was evaluated at least every four hours by focusing selected ion masses from perfluorokerosoene (PFK) and correcting the slope to account for minor variations. Mass focus stability was assured by the use of a reference PFK "lock mass" to correct for any mass focus drift.

Quantification

The PCDF/PCDD isomers were quantified by comparing the sum of the two ions monitored for each class to the sum of the two ions monitored for the corresponding internal standard. The 2,3,7,8-TCDF-$^{13}C_{12}$ was used to quantify the TCDF isomers, the 2,3,7,8-TCDD-$^{13}C_{12}$ was used to quantify the TCDD and the pentachloro through hexachloro isomers and the OCDD-$^{13}C_{12}$ used for the heptachloro through octachloro isomers. Experimental relative response factors were obtained by analyzing a test mix which contained representatives of the tetra- through octa-dioxin classes. These response factors were included in all calculations used to quantify the data. The response factors for the furans were assumed to be the same as those for the corresponding dioxin class. The response factors were calculated using the sum of the two ions monitored for each class of isomers compared to the sum of the two ions monitored for the corresponding internal standard. The experimental response factors were:

Tetra-CDF	0.980
Tetra-CDD	1.001
Penta	0.672
Hexa	0.570
Hepta	2.498
Octa	1.132

The formula used for quantifying the isomers was:

$$\text{Conc. (ng/g)} = \frac{\text{Areas of Quant. Masses}}{\text{Areas of Int. Std. Masses}} \times \frac{\text{Quant. of Internal Standard}}{\text{Resp. Factor} \times \text{1 g (for fuel oils)}}$$

In the case of the XAD-2 samples the level of PCDF/PCDD is reported in nanograms per total XAD-2 extract.

The criteria that were used to identify PCDD and PCDF isomers were:

(1) Simultaneous responses at both masses
(2) Isotope ratio within ± 15% of theoretical value
(3) Retention times within windows determined by analyses of standards
(4) Signal to noise ratio equal to or greater than 2.5 to 1

The 2,3,7,8-TCDF/TCDD isomers included the additional criterion that they coeluted within ± 1 second of their isotopically labelled analogs. A limit of detection was calculated for samples in which a particular chlorination class was not detected. The formula used was:

$$\text{Limit of Detection (ng/g)} = \frac{\text{Hts. of Quant. Masses}}{\text{Hts. of Int. Stnd. Masses}} \times \frac{\text{Quantity of Int. Std. x 2.5}}{\text{Resp. Factor x 1 g (for fuel oils)}}$$

In the case of the XAD-2 samples the limit of detection is reported in nanograms per total XAD-2 extract.

Results

The results from the PCDF/PCDD analyses are summarized in Tables 3 and 4 respectively. A detection limit is listed in parentheses for samples in which a particular chlorination class was not detected. The selected ion current traces for the sample and standard analyses are included in the appendix.

TABLE 1. HRGC/HRMS OPERATING PARAMETERS

Mass Resolution	9000-12000 (M/ΔM, 10% valley definition
Electron Energy	70 eV
Accelerating Voltage	6000 volts
Source Temperature	200°C
Preamplifier Gain	10^7 volts/amp
Electron Multiplier Gain	$\sim 10^6$
Transfer Line Temperature	280°C
Column	DB-5 30M
	CP Sil-88 50M
Injector Temperature	300°C
Column Temp - Initial (3 min)	160°C
Column Temp - Program	30°C/min
Column Temp - Final	250°C (CP Sil-88)
	290°C (DB-5)
Carrier Gas	Helium
Flow Velocity	~ 25 cm/sec
Injection Mode	Splitless
Injection Volume	2 µl

TABLE 2. EXACT MASSES USED FOR THE DETERMINATION OF PCDD AND PCDF

Compound	Accurate Mass Mass 1	Mass 2	Theoretical Isotope Ratio Mass 1/Mass 2
Monochlorodibenzo-p-dioxins	218.0134	220.0105	3.09
Monochlorodibenzofurans	202.0185	204.0156	3.09
Trichlorodiphenyl ethers	271.9562	273.9533	1.03
Dichlorodibenzo-p-dioxins	251.9745	253.9715	1.54
Dichlorodibenzofurans	235.9796	237.9766	1.54
Tetrachlorodiphenyl ethers	305.9173	307.9143	0.77
Trichlorodibenzo-p-dioxins	285.9355	287.9325	1.03
Trichlorodibenzofurans	269.9406	271.9376	1.03
Pentachlorodiphenyl ethers	341.8753	343.8724	1.54
Tetrachlorodibenzo-p-dioxins	319.8965	321.8936	0.77
Tetrachlorodibenzofurans	303.9016	305.8987	0.77
Hexachlorodiphenyl ethers	375.8364	377.8334	1.23
Pentachlodibenzo-p-dioxins	355.8546	357.8517	1.54
Pentachlorodibenzofurans	339.8597	341.8567	1.54
Heptachlorodiphenyl ethers	409.7974	411.7944	1.03
Hexachlorodibenzo-p-dioxins	389.8156	391.8127	1.23
Hexachlorodibenzofurans	373.8207	375.8178	1.23
Octachlorodiphenyl ethers	443.7584	445.7555	0.88
Heptachlorodibenzo-p-dioxins	423.7766	425.7737	1.03
Heptachlorodibenzofurans	407.7817	409.7788	1.03
Nonachlorodiphenyl ethers	477.7194	479.7165	0.77
Octachlorodibenzo-p-dioxin	457.7377	459.7347	0.88
Octachlorodibenzofuran	441.7428	443.7398	0.88
Decachlorodiphenyl ether	511.6805	513.6775	0.69

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

TABLE 3. LEVELS OF PCDF (DETECTION LIMIT)
WASTE FUELS (ppb) XAD-2 (ng/sample)

Sample	2,3,7,8-TCDF	Tetra-CDF	Penta-CDF	Hexa-CDF	Hepta-CDF	Octa-CDF
D1[a]	(0.129)	(0.129)	(0.063)	(0.094)	(0.909)	(1.999)
D2	(0.073)	(0.073)	(0.075)	(0.081)	(1.757)	(0.914)
E38	(0.066)	(0.081)	(0.055)	(0.080)	(0.881)	(1.113)
H	(0.050)	(0.050)	(0.074)	(0.146)	(0.667)	(0.881)
L2	(0.051)	(0.051)	(0.045)	(0.073)	(0.679)	(1.734)
MB[b]	(0.065)	(0.065)	(0.082)	(0.129)	(1.021)	(1.157)
XD1[c]	6.69	57.31	38.78	21.44	26.17	7.55
XD2	0.23	1.87	0.64	(0.333)	0.62	1.28
XE38	0.72	6.34	0.98	(0.260)	(2.586)	(2.198)
XH	(0.968)	(0.968)	3.56	10.24	1.99	5.25
XL2	0.29	5.34	4.36	5.43	3.26	2.98
XLB	(0.120)	(0.120)	(0.040)	(0.041)	(0.095)	(0.134)
MB	(0.182)	(0.182)	(0.087)	(0.186)	(0.389)	(1.497)

[a]D1 through L2 are waste fuel samples
[b]Laboratory Method Blank
[c]XD1 through XLB are flue gas extract samples

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)
24

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

TABLE 4. LEVELS OF PCDD (DETECTION LIMIT)
WASTE FUELS (ppb) XAD-2 (ng/sample)

Sample	2,3,7,8-TCDD	Tetra-CDD	Penta-CDD	Hexa-CDD	Hepta-CDD	Octa-CDD
D1[a]	(0.076)	(0.076)	(0.057)	(0.076)	(0.693)	(2.063)
D2	(0.072)	(0.072)	(0.075)	(0.108)	(1.755)	(4.168)
E38	(0.070)	(0.068)	(0.066)	(0.094)	(1.032)	(2.106)
H	(0.075)	(0.075)	(0.084)	(0.089)	(0.702)	(1.145)
L2	(0.050)	(0.050)	(0.045)	(0.074)	(0.714)	(1.648)
MB[b]	(0.090)	(0.090)	(0.064)	(0.095)	(0.823)	(3.444)
XD1[c]	(0.106)	3.28	2.06	2.85	6.86	7.32
XD2	0.04	0.50	0.59	0.96	2.22	7.59
XE38	(0.174)	(0.174)	(0.296)	(0.280)	(2.471)	(3.913)
XH	(0.0492	(0.492)	(0.401)	(0.898)	(1.442)	(3.024)
XL2	(0.045)	4.92	0.09	0.57	1.06	2.52
XLB	(0.064)	3.77	(0.046)	(0.052)	(0.108)	(0.220)
MB	(0.198)	(0.198)	(0.089)	(0.170)	(0.738)	(1.450)

[a]D1 through L2 are waste fuel samples
[b]Laboratory Method Blank
[c]XD1 through XLB are flue gas extract samples

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cln.)
(4-76)

30